# PERFORMANCE TESTING OF HYDROGEN TRANSPORT MEMBRANES AT ELEVATED TEMPERATURES AND PRESSURES

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## ABSTRACT

The development of hydrogen transport ceramic membranes offers increased opportunities for hydrogen gas separation and utilization. Commercial application of such membranes will most likely take place under conditions of elevated temperature and pressure, where industrial processes producing and or utilizing hydrogen occur, and where such membranes are theoretically expected to have the greatest permeability. Hydrogen separation membrane performance data at elevated temperature is quite limited, and data at elevated pressures is conspicuously lacking. This paper will describe the design, construction, and recent experimental results obtained from a membrane testing unit located at the U.S. Department of Energy⎕s Federal Energy Technology Center (FETC). The membrane testing unit is capable of operating at temperatures up to 900°C and pressures up to 500 psi. Mixed-oxide ceramic ion-transport membranes, fabricated at Argonne National Laboratory (ANL), were evaluated for hydrogen permeability and characterized for surface changes and structural integrity using scanning electron microscopy/ X-ray microanalysis (SEM/EDS), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), as a function of temperature, pressure, and hydrogen exposure.

## INTRODUCTION

The demand for hydrogen is expected to rise in coming years with increases in its use both directly as a fuel and indirectly in the synthesis or upgrading of fuels required to meet increasingly more demanding environmental standards. However, inexpensive and abundant sources of hydrogen, such as coal gasification, natural gas reforming, and off-gas streams from various process industries, usually contain hydrogen mixed with other gases. Recovery of hydrogen from these dilute streams would increase hydrogen supplies, improve overall process efficiencies, and provide a key component in the development of Integrated Gasification Combined Cycle (IGCC) power systems, fuel cells, advanced transportation fuel technology development, and ⎕Vision 21⎕ combination power and fuel production facilities. Advances in the area of membrane technology may provide the basis for improved methods of hydrogen recovery and thus reduce the cost associated with hydrogen production. Properly designed hydrogen membranes could be used to tailor syngas feed composition to optimize reactions producing fuel and/or chemical products.[1]

Currently, several research organizations are engaged in the development of hydrogen transport membranes or their precursor materials.[2] Membrane materials range from organic polymers to metals to ceramics. Non-porous ceramic membranes are particularly desirable because they can be made exclusively selective to hydrogen and are durable enough to withstand the harsh conditions of temperature, pressure, and chemical exposure that would probably be encountered in commercial application. Practical application of these membranes would likely employ a high total pressure on the retentate (inlet) side coupled with reduced pressures on the permeate (outlet) side to enhance the flux. Hydrogen flux through these membranes is expected to be optimal in the range of 700-900°C and increase with increasing hydrogen partial pressure gradient across the membrane. However, obtaining characterization information at these conditions is difficult, and data at elevated pressures (and pressure drops) is particularly scarce. The goal of the current work is to measure and characterize membrane performance at these elevated temperature and pressure conditions.

**EXPERIMENTAL SECTION**

Non-porous ceramic disk membranes were fabricated by a process developed at Argonne National Laboratory (ANL). Membranes used in this study were of composition $BaCe_{0.80}Y_{0.20}O_3$ (BCY), prepared by mixing appropriate amounts of $BaCO_3$, $CeO_2$, and $Y_2O_3$, then calcining the mixture at 1000°C for 12 h in air. This powder was then ball-milled and calcined again at 1200°C for 10 h in air. After obtaining phase-pure powder (by x-ray diffraction), the BCY powder was mixed with 40 vol.% metallic nickel powder to increase its electronic conductivity. The powder mixture was then uniaxially pressed and sintered for 5 h at 1400-1450°C in an atmosphere of 4% hydrogen/balance argon.

Membranes for pressure and flux testing were mounted using a brazing process developed at ANL, in 0.75" O.D. Inconel 600 tubing that had been drilled out to form a small seat to accommodate the membrane. Unmounted membranes of the same composition were also supplied for characterization studies. Because the pressure tested membranes had to be pre-mounted, the before-and-after characterization studies refer to membranes of the same composition and fabrication, but *not* the same physical membranes.

Membrane pressure and flux testing was performed on the Hydrogen Technology Research (HTR) facility, currently under construction at FETC. The facility makes use of high pressure hydrogen handling infrastructure previously put in place for the study of high pressure hydrogenation reactions.[3] For membrane testing, the unit has an operating range to 900°C temperature and 500 psig pressure (and pressure drop). The Inconel tubing containing the pre-mounted membrane from ANL was welded to an additional length of 0.75" O.D. Inconel 600 tubing. The membrane was hung in an inverted configuration and attached to a second piece of 0.75" OD Inconel tubing by means of a 0.75" I.D x 1.125" O.D. x 3.125" long Inconel 600 sleeve. A ceramic fiber heater was positioned around the sleeve. The entire assembly was suspended within a 2 gallon stainless steel autoclave under nitrogen gas. A simplified drawing of the test assembly is shown in Figure 1. Inert gas pressure tests were performed using static pressure by pressurizing the portion of the tubing and sleeve below the membrane, i.e., forcing the membrane *onto* the seat of the tubing. For inert gas testing only, the upper (permeate) side of the membrane was left exposed to air and monitored for leaks by means of a bubbler. Pressure was stepped in approximately 50 psi increments with hold times of approximately 0.5 h between increments. For hot tests, heat up and cool down was performed at the rate of 120°C per hour while at a slight inert gas over pressure. Pressure was increased only after the unit had obtained target temperature. When the unit is completed, hydrogen flux measurements will be

performed in a similar configuration, except that air will be totally excluded from the system and the reactor casing will be actively purged with nitrogen gas. The permeate side of the membrane will be swept with argon gas, and the effluent will be monitored with a gas chromatograph for hydrogen concentration.

Atomic Force Microscopic (AFM) images of the membrane were obtained using a Quesant Instrument Corporation AFM (Model-Resolver). X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Physical Electronics model 548 XPS system. The binding energies were referenced to the C(1s) level at 284.6 eV for adventitious carbon. XPS data were obtained at various temperatures ranging from room temperature to 650°C. X-ray microanalysis was performed at room temperature and 575°C using a JOEL 840-A scanning electron microscopy equipped with a Noran Instruments Micro-Z energy dispersive spectrometer, which was interfaced to a Noran Instruments Voyager-4. Detector resolution, as referenced to the Manganese K$\alpha$ spectra line, was 148 eV.

## RESULTS AND DISCUSSION

Cold membrane pressure tests were conducted using nitrogen and helium gases (separately) in the HTR unit. In each test, the ANL-1 disk membrane was pressurized in steps to 400 psig at ambient temperature. The membrane was held for approximately 0.5 h at each pressure and for 2 h at 400 psig. No leakage could be detected, either via a bubbler on the outlet side of the membrane, or via monitoring the pressure on the inlet side of the membrane. The pressure tests demonstrated that the membrane itself, as well as the ceramic-to-metal seal, was gas tight to 400 psig.

A hot membrane pressure test was conducted using nitrogen gas in the HTR unit. In this test, the ANL-1 disk membrane was heated to 800°C under a slight over pressure of nitrogen and held under these conditions for 17 h before pressure testing. During pressurization, no leakage could be detected up to and including 400 psig. At 450 psig, a small loss of pressure was observed together with bubble formation on the outlet side of the membrane. The leakage rate was measured at 1.6 mL/min at 450 psig. The leak persisted as the pressure was decreased in the same step wise fashion, although it slowly diminished in rate to 0.6 mL/min at 350 psig, and was undetectable at pressures below 200 psig. After decreasing to ambient pressure, the membrane was repressurized to 250 psig in the same step wise fashion and the leakage rate was confirmed. The membrane was again depressurized and cooled to ambient temperature. After cooling, the membrane was repressurized to 250 psig with cold nitrogen and the leakage rate was reconfirmed.

Following the hot membrane pressure test, visual inspection of the membrane revealed a powdery whitish coating on and around the membrane. Small areas of green discoloration were observed around the surface of the normally gray membrane. Some of the brazing material appeared to have migrated from around the edge of the membrane toward the center, moving a distance of approximately 0.5 mm. The braze migration had previously been observed during hot temperature-ambient pressure flux testing at ANL. Visual inspection under an optical microscope revealed cracks in the membrane surface along the perimeter of the disk, as well as cracks in the brazing material itself.

SEM/X-ray microanalysis was conducted to determine the changes in morphology, elemental distribution and compositional changes that occur to a fresh membrane upon heating. No major morphological changes were observed after heating the membrane from room temperature to 575°C.

Elemental distribution was uniform and remained uniform following heating and hydrogen exposures at 575°C.

SEM examination of the membrane before testing showed an apparent two phase structure of mixed Ba-Ce-Y oxides (spinodal decomposition appearance in the back scattered electron images) decorated with 2 - 20 μm ￼diameter￼ sized nickel-rich nodules (Figure 2, left image).  A similar image from the membrane after pressure testing is shown in Figure 2 (right image).  The nickel rich nodules seem to have grown in size during exposure to the test conditions.  The membrane surface also appeared to be covered by a film of some material on the side exposed to 450 psi nitrogen.

AFM was also utilized to determine both the surface morphology and the surface roughness.  AFM images of the fresh membrane and the membrane after the pressure test with nitrogen are shown in Figure 3.  The fresh membrane had structure containing nodules with an average surface height of 1.34 μ. The surface morphology changed after the pressure test. The original structure with nodules was not present after the pressure test and the average surface height was 1.89 μ.  This change in the surface roughness and morphology could be due to the deposition of carbon and other materials during mounting of the membrane, the nitrogen pressure test, or other associated handling.

XPS was utilized to determine the elemental composition and oxidation states of elements at approximately the top 50 Å of the surface of a fresh membrane upon heating.  Ni 2p spectra of the fresh membrane at room temperature and 650°C are shown in Figure 4.  At room temperature nickel was in the oxidized form and the intensity of the nickel peak was low. When the surface was heated up to 650°C, the intensity of the nickel peak increased substantially and the oxidation state of nickel changed to the metallic state. The ratios of Ni/Ba, Ni/Ce, and Ni/Y at the surface increased when the temperature was increased, but they decreased again when the surface was cooled back to room temperature.  Thus, the nickel  migrates to the surface and preferentially resides at the surface relative to the other elements at higher temperature. When the XPS analysis was performed at room temperature with the membrane after the pressure test, it was not possible to detect Ni, Ba, Ce, and Y on the surface. The intensity of the carbon peak was very high indicating that carbon may have been deposited on the surface during the pressure test.  When the surface was heated to 300°C, the intensity of the carbon signal decreased by 33% and a small amount of yttrium was detected on the surface.  When the surface was heated to 650°C, there was a 60% decrease in the amount of carbon, and it was possible detect all the elements on the surface.  The amounts of Ni and Y were higher on the surface relative to the other elements at 650°C.  This differs from the observations made with the fresh membrane at 650°C in which the concentrations of barium and nickel were higher than those of the other elements.

**CONCLUSION**

The membrane and sealing methodology are impermeable to the inert test gases nitrogen and helium.  In addition, both membrane and seal are structurally capable of withstanding a pressure differential of 400 psig, at least for the limited hold times employed in these tests.  However, at 800°C, the membrane and seal would not withstand a pressure of 450 psig nitrogen and developed a leak.  At this time, it is not known whether the failure was strictly a pressure effect, or if the elevated temperature and possible migration of some of the brazing material was involved.  It is likely that exposing the membrane to atmospheric oxygen on the permeate side contributed to its demise.  At high temperature, the membrane will also transfer oxygen, and the presence of what is probably oxide contamination around the membrane after the hot pressure test indicates that some degradation of

the membrane and/or sealing materials may have occurred during the test.  Both SEM and AFM indicated that the pressure tested membrane surface was coated with an impurity material, although it cannot be determined whether this occurred as a direct result of the pressure test or from other handling or exposure.  XPS analysis indicates that significant elemental and oxidative changes occurred on the membrane surface upon heating.  In particular, pools of metalic nickel migrated to the membrane surface at elevated temperature.  The nickel islands may very well contribute to the ability of the membrane to transfer hydrogen by facilitating molecular dissociation.  However, such changes may also affect membrane strength.  High temperature-high pressure hydrogen flux measurements for these membranes are of great interest and should be obtainable shortly.

## ACKNOWLEDGEMENTS

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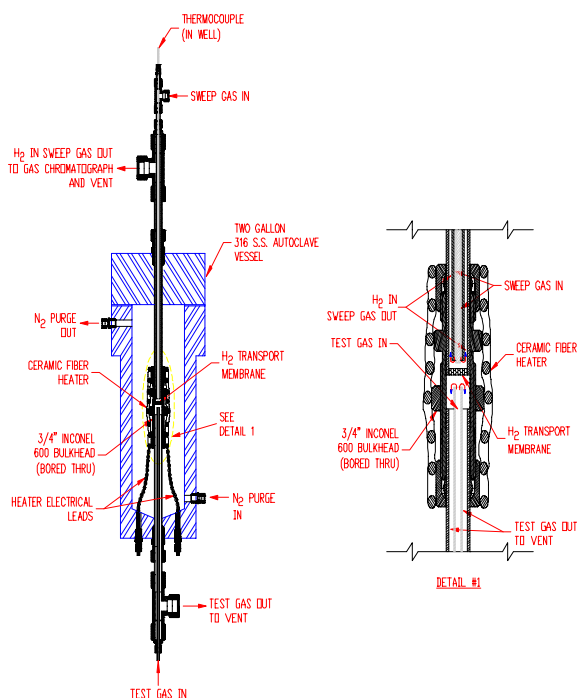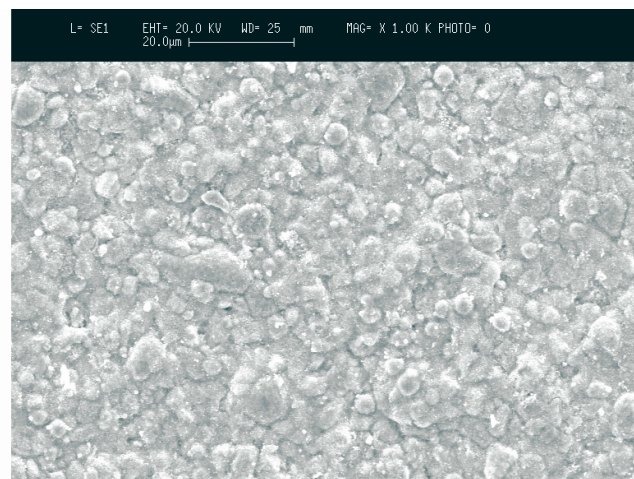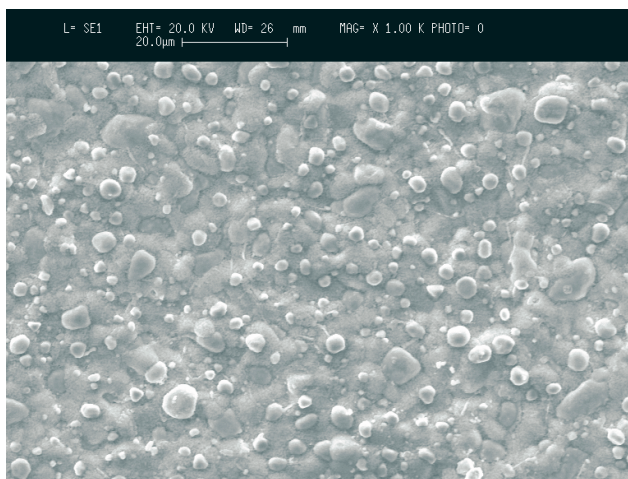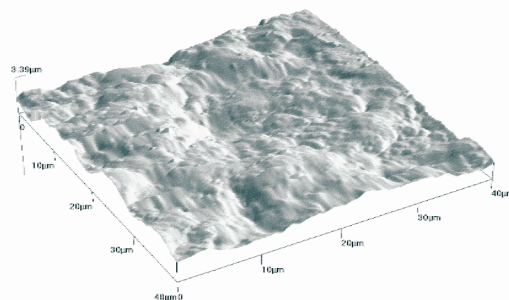
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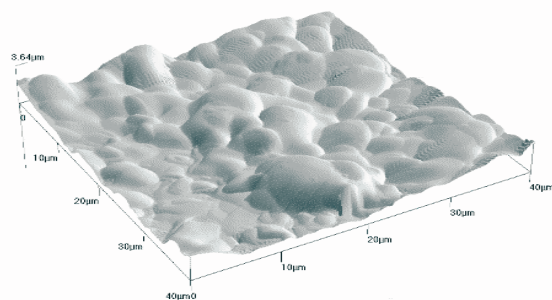


(a) Fresh Membrane

(b) Membrane after Pressure Test

Ni 2p Spectra of Membranes